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| (54) Title: COOLANT COMPOSITIONS | | |
| (57) Abstract The present invention relates to compositions comprising a suitable carrier and a coolant combination of a glycol and a coolant and wherein the pH of said compositions is greater than about 8.2 in the composition itself or when used. | | |

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COOLANT COMPOSITIONS

BACKGROUND

Compositions of various types have incorporated within them components which provide cooling sensation to mucosal membranes and/or to skin. Such compositions include toothpastes, mouthwashes, perfumes, lotions, shaving cream, post shaving preparations, shampoos, antiperspirants, deodorants, beverages, chewing gum, tobacco products, and pharmaceutical products among many others.

It is well established that the "cooling" effect of menthol is a physiological effect due to the direct action of menthol on the nerve endings of the human body responsible for the detection of hot or cold and is not due to latent heat of evaporation. It is believed that the menthol acts as a direct stimulus on the cold receptors at the nerve endings which in turn stimulate the central nervous system.

Although menthol is well established as a physiological coolant, its use alone, in some compositions, is limited by its strong minty odor and its relative volatility.

Several other compounds have been reported in the technical literature as having an odor or flavor similar to menthol and from time to time have been proposed as flavorants or odorants in a variety of topical and ingestible compositions. For example, Japanese Patent Publication No. 39-19627 reports that 3-hydroxymethyl p-menthane (menthyl carbinol) has a flavor closely resembling that of 1-menthol and suggests its use as a flavorant in confectionery, chewing gum and tobacco. In Swiss Patent No. 484,032 certain saccharide esters of menthol are proposed as additives to tobacco. In French Pat. Spec. No. 1,572,332 N,N-Dimethyl 2-ethylbutanamide is reported as having a minty odor and refreshing effect, and the minty odor of N,N-diethyl 2,2-dimethylpropanamide is referred to. A similar effect is reported for N,N-diethyl 2-ethylbutanamide in Berichte 39, 1223, (1906). A minty odor has also been reported for 2,4,6-trimethylheptan-4-ol and 2,4,6-trimethyl hept-2-en-4-ol in Parfums-Cosmetiques-Savons, May 1956, pp. 17-20. The cooling effect of menthol and other related terpene alcohols and their derivatives have also been studied and reported in Koryo, 95, (1970), pp. 39-43. 2,3-p-menthane diol has also been reported as having a sharp cooling taste (Beilstein,

Handbuch der Organischen Chemie, 4th Ed. (1923) Vol. 6, p. 744).

Carboxamides have also been disclosed for use in a variety of compositions. Two patents describing such materials and compositions are U.S. 4,136,163, January 23, 1979 to Watson, et al. and U.S. 4,230,688, October 28, 1980 to Rowsell, et al. These patents as well as those set forth above are incorporated herein in their entirety by reference.

Although there have been these significant efforts to provide enhanced cooling properties to a wide variety of products there is still the need to provide improved performance, including a greater perception of a clean feel.

It is an object therefore of the present invention to provide improved compositions using improved coolant compositions.

It is a further object to provide improved coolant compositions comprising a glycol and a coolant wherein the pH is greater than about 8.2.

It is a further object of the present invention to provide improved coolant compositions comprising a glycol, a carboxamide, and a secondary coolant.

These and other objects of the present invention are described in detail below.

All measurements referred to herein are made at 25°C and all percentages are by weight unless otherwise specified.

SUMMARY OF THE INVENTION

The present invention includes compositions comprising a suitable carrier, a glycol, and a coolant wherein the pH of said compositions is greater than about 8.2. Methods of providing cooling are also included within the scope of this invention.

DETAILED DESCRIPTION OF THE INVENTION

The components of the present invention are described in detail below.

Glycol:

The use of the term "glycol" in this application is meant to include any glycol which is suitable for use on the skin, mucosal surfaces such as in the oral cavity or ingested. Suitable glycols include propylene glycol, butylene glycol, hexylene glycol and mixtures thereof, among others. The preferred glycol is propylene glycol.

The glycol materials, when used alone or in combination, are present at a level in the composition of from about 0.1% to about 10%, preferably

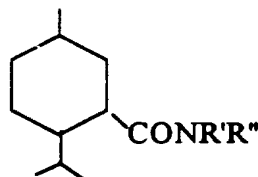
from about 1% to about 8%, most preferably from about 2% to about 6%.

Coolant:

The second required component of the present invention is a coolant. The coolant can be any of a wide variety of materials. Included among such materials are carboxamides.

The carboxamides found most useful in the present invention are those described in U.S. Patent 4,136,163, January 23, 1979 to Watson, et al. and U.S. Patent 4,230,688, October 28, 1980 to Rowsell, et al., both incorporated herein by reference in their entirety.

The carboxamides in the '163 patent are N-substituted-p-menthane-3-carboxamides. These compounds are 3-substituted-p-menthanes of the formula:



where R', when taken separately, is hydrogen or an aliphatic radical containing up to 25 carbon atoms; R'' when taken separately is hydroxy, or an aliphatic radical containing up to 25 carbon atoms, with the proviso that when R' is hydrogen R'' may also be an aryl radical of up to 10 carbon atoms and selected from the group consisting of substituted phenyl, phenalkyl or substituted phenalkyl, naphthyl and substituted naphthyl, pyridyl; and R' and R'', when taken together with the nitrogen atom to which they are attached, represent a cyclic or heterocyclic group of up to 25 carbon atoms, e.g., piperidino, morpholino, etc.

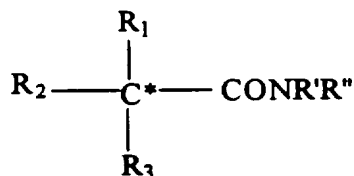
In the above definitions "aliphatic" is intended to include any straight-chained, branched-chained or cyclic radical free or aromatic unsaturation, and thus embraces alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, hydroxyalkyl, acyloxyalkyl, alkoxy, alkoxyalkyl, aminoalkyl, acylaminoalkyl, carboxyalkyl and similar combinations.

Typical values for R' and R'' when aliphatic are methyl, ethyl, propyl, butyl, isobutyl, n-decyl, cyclopropyl, cyclohexyl, cyclopentyl, cycloheptylmethyl, 2-hydroxyethyl, 3-hydroxy-n-propyl, 6-hydroxy-n-hexyl, 2-aminoethyl, 2-acetoxyethyl, 2-ethylcarboxyethyl, 4-hydroxybut-2-ynyl, carboxymethyl etc.

When R'' is aryl typical values are benzyl, naphthyl, 4-methoxyphenyl, 4-hydroxyphenyl, 4-methylphenyl, 3-hydroxy-4-methylphenyl, 4-

fluorophenyl, 4-nitrophenyl, 2-hydroxynaphthyl, pyridyl, etc.

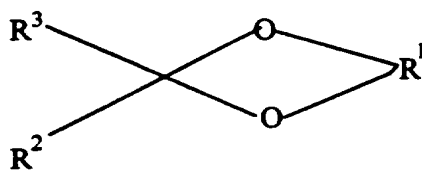
The carboxamides of the '688 patent are certain acyclic tertiary and secondary carboxamides. These have the structure



where R' and R'', when taken separately, are each hydrogen, C₁-C₅ alkyl or C₁-C₈ hydroxyalkyl and provide a total of no more than 8 carbon atoms, with the proviso that when R' is hydrogen R'' may also be alkylcarboxyalkyl of up to 6 carbon atoms;

R' and R'', when taken together, represent an alkylene group of up to 6 carbon atoms, the opposite ends of which group are attached to the amide nitrogen atom thereby to form a nitrogen heterocycle, the carbon chain of which may optionally be interrupted by oxygen;

R₁ is hydrogen or C₁-C₅ alkyl; and R₂ and R₃ are each C₁-C₅ alkyl; with the provisos that (i) R₁, R₂ and R₃ together provide a total of at least 5 carbon atoms, preferably from 5-10 carbon atoms; and (ii) when R₁ is hydrogen, R₂ is C₂-C₅ alkyl and R₃ is C₁-C₅ alkyl and at least one of R₂ and R₃ is branched, preferably in an alpha or beta position relative to the carbon atom marked (*) in the formula. Additional coolants include such materials as ketals, menthol, and diols. Preferred ketals for use in the present invention have the formula



(I)

in which R¹ represents a C₁-C₆-alkylene radical having at least 1, but not more than 3, hydroxyl group(s), preferably 1 hydroxyl group, and either R² and R³ independently of one another represent C₁-C₁₀-alkyl which is optionally substituted by 1 to 3 radicals selected from the group comprising hydroxyl, amino and halogen (such as fluorine, chlorine, bromine or iodine), C₅-C₇-cycloalkyl, preferably cyclohexyl, C₆-C₁₂-aryl, preferably phenyl, with the proviso that the total of the C atoms of R² and R³ is not less than 3, or R² and R³ together represent an alkylene radical which, together with

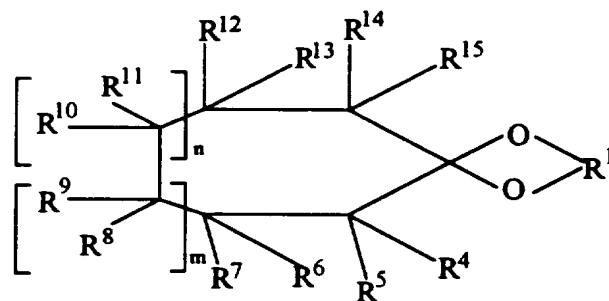
the carbon atom which carries the radicals R^2 and R^3 , forms a 5-7-membered ring, it being possible for this alkylene radical, in turn, to be substituted by C_1 - C_6 -alkyl groups.

Preferred radicals R^2 and R^3 comprise methyl, isopropyl and tert.-butyl.

The length of the radicals R^2 and R^3 influences the effect of the compounds I: shorter radicals lead to an immediate, short effect; longer radicals lead to a delayed, but prolonged effect. An important aspect for the cosmetics industry is the solubility of the compounds in water; this is the case, in particular, with short radicals R^2 and R^3 .

Preferred radicals R^1 embrace 1,2- and 1,3-alkylene radicals which, together with the two oxygen atoms and with the carbon atom to which the two oxygen atoms are attached, form a dioxolane or dioxane ring.

Preferred compounds I in which R^2 and R^3 together represent an alkylene radical are those of the formula



(Ia)

in which R^4 to R^{15} independently of one another denote hydrogen or C_1 - C_6 -alkyl, preferably hydrogen or C_1 - C_4 -alkyl, and m and n independently of one another denote zero or 1.

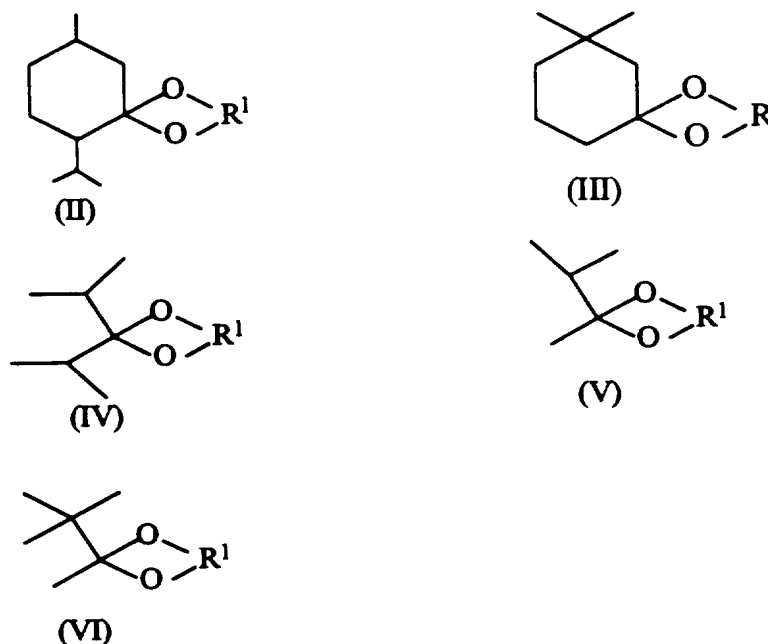
Preferred compounds of the formula Ia are those in which the total of $m + n$ is 1, i.e. ketals of an optionally substituted cyclohexanone.

Preferred substituents, of which there may be present, in particular, 1 to 3, are methyl, isopropyl and tert.-butyl.

The ketals I can be prepared by known processes. For example, ketal I will generally be prepared by acid-catalysed reaction of the ketone on which ketal I is based and not less than the equivalent amount of aliphatic C_3 - C_6 -alcohol having not less than 3 and not more than 5, preferably 3, hydroxyl groups. In general, the ketone on which ketal I is based and not less than 0.5 mol equivalents, but, as a rule, a 1.2- to 4-fold, preferably 1.5- to 3-fold excess of this amount of the C_3 - C_6 -alcohol having

3 to 5 hydroxyl groups will be employed. Examples of acid catalysts which can be used are p-toluenesulphonic acid, phosphoric acid or potassium hydrogen sulphate in catalytically effective amounts (for example 0.1 to 3 g of p-toluenesulphonic acid per mole of ketone). The reaction will preferably be carried out either in an organic solvent which together with water forms an azeotrope, so that the water, which is liberated during the formation of the ketal, can be eliminated by azeotropic entrainment, or water-consuming coreagents such as, for example, trialkyl ortho esters are used. Examples of preferred organic solvents comprise benzene, toluene, xylene, chloroform, methylene chloride and trichloroethylene.

The reaction can be regarded as complete when water no longer separates out or when an ester/alcohol mixture is no longer separated out. It is recommended to wash the products subsequently with dilute alkali and with water, to separate and dry the organic phase, to strip off the solvent and, if appropriate, to purify the residue, for example by distillation. Particularly preferred ketals I are those of the formulae



in which R^1 has the above mentioned meaning, particularly preferred substances from among the ketals II to VI being in each case the glycerol ketals.

The invention also relates to the ketals III to VI. The ketals I to be employed in the compositions according to the invention can have

asymmetric C atoms; optical isomerism can therefore occur. Depending on the starting material and the preparation methods used, they can exist in the form of mixtures of the optical isomers or in the form of pure isomers. The cooling effect of the isomers may differ, so that one or the other isomer may be preferred.

Menthol is another coolant which may be used in the present invention. Menthol is a component of peppermint oil and is widely used in oral care products, food stuffs, and cosmetics.

Yet another suitable secondary coolant is a diol. Preferred diols are those set forth in U.S. Patent 4,459,425 to Amano et al, July 10, 1984, incorporated herein in total by reference. A preferred diol is 3-1-methoxy propane-1,2-diol.

The coolant compounds can be used in any effective amount in the present compositions. Generally the level in the compositions is from about 0.01% to about 1%, preferably from about 0.05 % to about 0.60%, more preferably from about 0.07% to about 0.29%.

Carrier:

The compositions in which the aforescribed coolant materials find application are many and varied. These compositions include a wide variety of compositions for consumption by or application to the human body. Broadly speaking, these compositions can be divided into comestible and topical compositions, both terms being taken in their broadest possible sense. Thus comestible is to be taken as including not only foodstuffs and beverages taken into the mouth and swallowed, but also other orally ingested compositions taken for reasons other than their nutritional value, e.g., ingestion tablets, antacid preparations, laxatives etc. Comestible compositions also include edible compositions taken by mouth, but not necessarily swallowed, e.g. chewing gum. Topical compositions include not only compositions such as perfumes, powders and other toiletries, lotions, liniments, oils and ointments applied to the external surfaces of the human body, whether for medical or other reasons, but also compositions applied to, or which, in normal usage, come in contact with internal mucous membranes of the body, such as those of the nose, mouth, or throat, whether by direct or indirect application or inhalation, and thus include nasal and throat sprays, dentifrice, mouthwash and gargle compositions. Also included within the present invention are toilet articles such as cleansing tissues and toothpicks impregnated or coated with the active

cooling compound.

A further class of compositions included within the scope of this invention are tobacco and associated articles e.g. pipe and cigarette filters, especially filter tips for cigarettes.

In formulating the compositions of this invention the cooling compositions will usually be incorporated into a carrier which may be completely inert or which may be or contain other active ingredients. A wide variety of carriers will be suitable, dependent upon the end use of the composition, such carriers including solids, liquids, emulsions, foams and gels. Typical carriers for the cooling compositions include aqueous or alcoholic solutions; oils and fats such as hydrocarbon oils, fatty acid esters, long chain alcohols and silicone oils; finely divided solids such as starch or talc; cellulosic materials such as paper tissue; tobacco; low-boiling hydrocarbons and halohydrocarbons used as aerosol propellents; gums and natural or synthetic resins.

The following illustrate the range of compositions into which the cooling compositions can be incorporated:

1. Edible or potable compositions including alcoholic and non-alcoholic beverages, confectionery, frostings, chewing gum; cachous; ice cream; jellies.
2. Toiletries including after shave lotions, shaving soaps, creams and foams, toilet water, deodorants and antiperspirants, "solid colognes", toilet soaps, bath oils and salts, shampoos, hair oils, talcum powders, face creams, hand creams, sunburn lotions, cleansing tissues, dentifrices, toothpicks, dental floss, toothbrushes, mouthwashes, hair tonics, denture adhesives.
3. Medicaments including antiseptic ointments, liniments, lotions, decongestants, counter-irritants, cough mixtures, throat lozenges, antacid and indigestion preparations, oral analgesics.
4. Tobacco preparations including cigars, cigarettes, pipe tobacco, chewing tobacco and snuff; tobacco filters, especially filter tips for cigarettes.
5. Miscellaneous compositions such as water soluble adhesive compositions for envelopes, postage stamps, adhesive labels etc.

Particular preparations according to the invention are discussed in more detail below.

Edible and Potable Compositions:

The edible and potable compositions of this invention will contain the cooling composition in combination with an edible carrier and usually a flavoring or coloring agent. The particular effect of the cooling compounds is to create a cool or fresh sensation in the mouth, and in some cases even in the stomach, and therefore the compositions find particular utility in sugar-based confectionery such as chocolate, boiled sweets and candy, in ice cream and jellies and in chewing gum. The formulation of such confections will be by ordinary techniques and according to conventional recipes and as such forms no part of this invention. The coolant composition will be added to the final composition at a convenient point and in amount sufficient to produce the desired cooling effect in the final product. As already indicated, the amount will vary depending upon the particular composition, the degree of cooling effect desired and the strength of other flavorants in the composition.

Similar considerations apply to the formulation of beverages. Generally speaking the compositions will find most utility in carbonated or noncarbonated soft drinks e.g., fruit, lemonade, cola, etc., but may also be used in alcoholic beverages.

Toiletries:

Because of the cooling sensation imparted to the skin, a major utility of the cooling compositions will be in a wide range of toilet preparations and toilet articles. The particular preparations discussed below are to be taken as exemplary.

A major utility will be in after shave lotions, toilet water etc., where the compounds will be used in alcoholic or aqueous alcoholic solution, such solutions usually also containing a perfume or mild antiseptic or both.

Another field of utility will be in soaps, shampoos, bath oils etc. where the compositions will be used in combination with an oil or fat or a natural or synthetic surfactant e.g., a fatty acid salt or a lauroylsulphate salt, the composition usually also containing an essential oil or perfume. The range of soap compositions will include soaps of all kinds, e.g., toilet soaps, shaving soaps, shaving foams etc.

A further class of toilet compositions into which the compositions may be incorporated includes cosmetic creams and emollients, such creams and emollients usually comprising a base emulsion and optionally a range of ingredients such as wax, preservative, perfume, antiseptics, astringents,

pigments etc. Also included within this class are lipstick compositions, such compositions usually comprising an oil and wax base into which the coolant compositions can be incorporated along with the conventional ingredients, i.e., pigments, perfumes etc. Once again the formulation of such compositions is conventional.

Compositions for oral hygiene containing the cooling compositions include mouthwash and dentifrice compositions and are preferred compositions. The first will usually comprise an aqueous, alcoholic, or aqueous-alcoholic solution of an antiseptic often colored or flavored for palatability in an amount of from 0.1% to 1.0% by weight.

Dentifrice compositions may be of the powder, paste or liquid type and will usually comprise a finely divided abrasive or polishing material, e.g., precipitated chalk, silica, magnesium silicate, aluminum hydroxide or other similar materials well known in the art, and a detergent or foaming agent. Optional ingredients which may also be included are flavoring agents and colorants, antiseptics, lubricants, thickeners, emulsifiers or plasticizers.

Other optional components useful in the present invention are pyrophosphate salts such as those described in U.S. 4,515,772, May 7, 1985 to Parran et al, incorporated herein by reference. Also useful are nonionic antimicrobials such as triclosan described in U.S. 4,894,220, January 16, 1990 to Nabi, et al. Both patents are incorporated herein by reference. Examples of such agent include triclosan and other phenolic compounds.

Another agent which can be used in the present compositions is an alkali metal bicarbonate such as sodium bicarbonate. These are stable items of commerce and can be used together with a peroxide compound in separate compartments such as disclosed in U.S. 4,849,213 and U.S. 4,528,180, both to Schaeffer, incorporated herein by reference in its entirety.

The preferred coolant blends useful in oral compositions include mixtures of one or more carboxamides with the glycol. The preferred levels of coolants are from about 0.0500 to about 0.2000 for the coolants of the '688 patent and from about 0.0500 to about 0.1000 of the '163 patent coolants.

Medicaments:

Because of their cooling effect on the skin and on the mucous

membranes of the mouth, throat and nose and of the gastrointestinal tract the cooling compositions may be used in a variety of oral medicines, nasal and throat sprays, and topical compositions, particularly where a counter-irritant is required. In particular the coolant compositions may be formulated into antacid and indigestion remedies, in particular those based on sodium bicarbonate, magnesium oxide, calcium or magnesium carbonate, aluminum or magnesium hydroxide or magnesium trisilicate.

The coolant compositions may also be included in oral analgesic compositions e.g. with acetylsalicylic acid or its salts, acetamenophin, ibuprofen, naproxen, as well as other propronic derivatives, and in nasal decongestants, e.g., those containing ephedrine.

Certain compositions of this invention are illustrated by the following non-limiting examples. These examples are strictly given for illustration purposes and are not limiting of the invention described herein as many variations are possible without departing from the spirit and scope of the invention as set forth herein..

EXAMPLE 1

Given below is an exemplary toothpaste composition representative of the present invention.

| <u>Component</u> | <u>Weight %</u> |
|--------------------------------|-----------------|
| Sorbitol | 52.512 |
| Silica | 20.000 |
| Water | 11.165 |
| Propylene Glycol | 5.000 |
| Synthetic Sodium Alkyl Sulfate | 4.000 |
| Sodium Bicarbonate | 1.500 |
| Trisodium Phosphate | 1.450 |
| Flavor | 1.000 |
| Sodium Hydroxide | 0.600 |
| Monosodium Phosphate | 0.590 |
| Titanium Dioxide | 0.525 |
| Sodium Fluoride | 0.243 |
| Xanthan Gum | 0.475 |
| Sodium Saccharin | 0.350 |
| Carbopol | 0.300 |
| WS-23 ¹ | 0.200 |
| WS-3 ² | 0.090 |

¹ U.S. Patent 4,136,163, January 23, 1979, to Watson, et al.

² U.S. Patent 4,230,688, October 28, 1980, to Rowsell, et al.

EXAMPLES 2-5

Given below are additional toothpastes.

| <u>Composition</u> | <u>2</u> <u>Weight %</u> | <u>3</u> <u>Weight %</u> | <u>4</u> <u>Weight %</u> | <u>5</u> <u>Weight %</u> |
|--------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Sorbitol | 52.512 | 47.223 | 22.514 | 39.750 |
| Silica | 20.000 | 20.00 | 22.500 | 15.000 |
| Water | 11.165 | 10.201 | 23.261 | 10.000 |
| Propylene Glycol | 5.000 | 5.000 | 5.000 | 5.000 |
| Synthetic Sodium Alkyl Sulfate | 4.000 | 5.000 | 4.000 | 4.000 |
| Sodium Bicarbonate | 1.500 | 1.500 | 1.500 | 20.000 |
| Tri Sodium Phosphate | 1.450 | 1.330 | | |
| Flavor | 1.000 | 0.963 | 0.900 | 1.000 |
| Sodium Hydroxide | 0.600 | 0.600 | 0.600 | |
| Monosodium Phosphate | 0.590 | 0.800 | | |
| Titanium Dioxide | 0.525 | 0.500 | | 0.350 |
| Xanthan Gum | 0.475 | | 0.600 | |
| Sodium Saccharin | 0.350 | 0.330 | 0.460 | 0.517 |
| Carbopol | 0.300 | 0.220 | 0.200 | |
| WS-23 | 0.200 | 0.200 | 0.200 | 0.200 |
| WS-3 | 0.090 | 0.090 | 0.090 | 0.090 |
| Sodium Fluoride | 0.243 | 0.243 | 0.243 | 0.243 |
| Glycerin | | 5.000 | 4.000 | 2.000 |
| Tetrapotassium Pyrophosphate | | | 6.382 | |
| PEG 300 | | | 3.000 | |
| Sodium Acid Pyrophosphate | | | 2.100 | |
| Tetrasodium Pyrophosphate | | | 2.050 | |
| FD&C Blue #1 | | 0.050 | 0.400 | |
| Sodium Carbonate | | | | 1.000 |
| Carboxymethyl Cellulose | | 0.750 | | 0.850 |

EXAMPLE 6

Given below is a mouthrinse example representative of the present invention.

| <u>Component</u> | <u>Weight %</u> |
|------------------|-----------------|
| Glycerin | 7.5000 |
| Flavor | 0.1200 |
| Benzoic Acid | 0.0030 |
| Ethanol | 8.5000 |
| Polysorbate 80 | 0.1200 |
| Poloxomer 407 | 0.2000 |
| Water | 82.7291 |
| WS-23 | 0.0500 |
| WS-3 | 0.0250 |

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| | |
|--------------------------|--------|
| Propylene Glycol | 1.2500 |
| Sodium bicarbonate | 0.3750 |
| Domiphen Bromide | 0.0050 |
| Cetylpyridinium Chloride | 0.0450 |
| Sodium Saccharin | 0.0765 |
| Color | 0.0014 |

EXAMPLE 7

Given below is an example of a throat drop representative of the present invention.

| <u>Component</u> | <u>Weight %</u> |
|--------------------|-----------------|
| Propylene Glycol | 0.500 |
| Sodium Bicarbonate | 0.200 |
| WS-23 | 0.020 |
| WS-3 | 0.015 |
| Throat Drop Base | q.s. 100.000 |

EXAMPLE 8

Given below is an example of a chewing gum representative of the present invention.

| <u>Component</u> | <u>Weight %</u> |
|--------------------|-----------------|
| WS-23 | 0.200 |
| WS-3 | 0.090 |
| Propylene Glycol | 2.000 |
| Sodium Bicarbonate | 1.500 |
| Chewing Gum Base | q.s. 100.000 |

WHAT IS CLAIMED IS:

1. A composition comprising a glycol selected from the group consisting of propylene glycol, butylene glycol, hexylene glycol, and mixtures thereof; a coolant material; and a suitable carrier composition wherein the pH of said composition is greater than 8.2, either as measured in the composition itself or when used.
2. A composition according to Claim 1 wherein the coolant is selected from the group consisting of carboxamides, menthol, ketals, diols, and mixtures thereof.
3. A composition according to either of Claim 1 or 2 which contains a bicarbonate salt as a pH adjustment agent.
4. A composition according to any of Claims 1-3 which contains a bicarbonated salt as a pH adjustment agent.
5. A composition according to any of Claims 1-4 in which the coolant is a carboxamide.
6. A composition according to any of Claims 1-5 which is in the form of a toothpaste.
7. A composition according to any of Claims 1-6 which additionally contains an abrasive.
8. A composition according to any of Claims 1-7 which additionally contains a soluble fluoride ion source.
9. A composition according to Claim 4 wherein the abrasive is a silico abrasive.
10. A composition according to Claim 4 which is in the form of a mouthrinse.
11. A composition according to any of Claims 1-4 which is in the form of a cough drop.

12. A composition according to any of Claims 1-4 which is in the form of a chewing gum.
13. A composition according to Claim 8 wherein the composition of Claim 8 which in addition contains a bicarbonate salt and is present as one part of a codispensing container and the other part of the container contains a peroxide source.

INTERNATIONAL SEARCH REPORT

Internat. Application No.
PCT/US 96/02257

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| A. CLASSIFICATION OF SUBJECT MATTER IPC 6 A61K7/00 A61K7/48 A61K7/16 A61K7/22 | | |
| According to International Patent Classification (IPC) or to both national classification and IPC | | |
| B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 A61K | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched | | |
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| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
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| <div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div> | | |
| <div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>* "A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>* "E" earlier document but published on or after the international filing date</p> <p>* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>* "O" document referring to an oral disclosure, use, exhibition or other means</p> <p>* "P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>* "&" document member of the same patent family</p> </div> </div> | | |
| Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">5 June 1996</div> | | Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">13. 06. 96</div> |
| Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016 | | Authorized officer <div style="text-align: center; font-weight: bold;">Luyten, H</div> |

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International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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